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HIGH TRANSPARENT CONDUCTIVE ALUMINUM-DOPED ZINC OXIDE THIN FILMS BY REACTIVE CO-SPUTTERING (POSTPRINT)

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Al-doped ZnO films were fabricated using reactive magnetron sputtering simultaneously using separate Zn and Al targets. The AZO films showed high transparency in the visible region and low transmittance in the near IR regions.

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High Transparent Conductive Aluminum-doped Zinc Oxide Thin Films by Reactive Co-Sputtering

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Abstract: Al-doped ZnO films were fabricated using reactive magnetron sputtering simultaneously using separate Zn and Al targets. The AZO films showed high transparency in the visible region and low transmittance in the near IR regions.

OCIS codes: (310.6860) Thin films; (310.7005) transparent conductive coatings; (310.1860) Deposition and fabrication

1. Introduction

Transparent conductive oxides, such as Al-doped zinc oxide (AZO) films, have showed excellent structural, optical and electric properties for applications of optoelectronic devices, solar cell, and heat reflecting coatings [1-4]. In the past, AZO films were fabricated by many techniques and their properties were studied such as pulse DC magnetron sputtering with an AZO target [1], RF multi-metallic-target reactive magnetron sputtering [2-3], RF and DC magnetron sputtering with ZnO and Al targets [5] and Al fragments on ZnO target [6].

In this work, AZO films were deposited by reactive magnetron co-sputtering two individual Zn and Al targets simultaneously in a mixture of O_2 and Ar. The Al doping content was adjusted by the sputtering powers on each target, the substrate temperature and target-to-substrate working distance (WD) without breaking vacuum. Their chemical composition, structural, optical and electrical properties were characterized and studied by XPS, XRD, spectroscopic ellipsometry, UV-Vis-NIR spectra and Four-Point-Probe.

2. Experimental details

The AZO films were fabricated using reactive magnetron co-sputtering in an O_2 and Ar plasma. The two metallic targets, Zn (50 mm diameter, purity 99.995%) and Al (50mm diameter, purity 99.95%) were powered simultaneously using a pulsed DC power supply and a DC power supply, respectively. The chamber base pressure was at 2.0 x 10^{-7} Torr using a turbomolecular pump. The operating pressure was kept at 3 mTorr with high purity argon gas (99.999%) at a fixed flow rate of 20 sccm. The gate valve was locked at this position before high purity oxygen gas (99.99%) at a 1.8 sccm flow rate was brought into the chamber. Quartz substrates were used on a rotated substrate holder and two target-to-substrate working distances (WD) - S (short) and L (long) were used. The films were also deposited on (100) silicon wafers for XPS characterizations. The deposition parameters are listed in Table 1.

Table 1 Deposition parameters.

Sample	Zn Power (W)	Al Power (W)	WD	T_s (˚C)
(a)	30	0	S	170
(b)	60	0	S	25
(c)	60	28	L	25
(d)	60	28	L	170
(e)	60	28	S	25
(f)	60	27	S	170

The spectroscopic ellipsometry data Psi and Delta at three incident angles of 50°, 55° and 60° as well as the Transmission Intensity in the wavelength range of 270-2500nm were performed using a J.A. Woollam VASE ellipsometer. The thickness and optical constants of the films were derived from fitting the experimental ellipsometry data Psi, Delta, and Transmission Intensity with a model containing one Tauc-Lorentz and two Lorentz oscillators. The UV-Vis-NIR transmittance spectra on quartz were performed in the wavelength range of 200-2500 nm using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The crystal structure of the films was analyzed by a

X-ray diffraction (XRD) measurement in 2θ/Ω scan mode using a Rigaku SmartLab x-ray diffractometer with a Cu Kα (λ = 1.541862 Å) x-ray source (40kV/44mA). The XRD measurements were scanned in a 2θ range of 20º-80º at a scan speed of 20º per minute with a step size of 0.01º. The electrical resistivity was determined by a Four-Point Probe (Four Dimensions USA, Six-Point-Probe Meter Model 101C) measurement. The XPS measurements were made using a PHI 5700 instrument with a monochromatic Al X-ray source.

3. Results and Discussions

As shown in Figure 1, the XRD patterns indicate that all AZO films (a) to (f) were in hexagonal Wurtzite ZnO structure with a highly preferred orientation of (002). The 2θ position of (002) and their full width half maxima (FWHM) as well Al doping (Al/(Al+Zn) ratio) from XPS are listed in Table 2. The FWHM decreased at the high Zn sputtering power of 60W and further decreased with Al doping. Therefore the crystallinity was enhanced with Al doping. In figure 2 of the UV-Vis-NIR transmittance spectra, the transmittance in the near IR (NIR) decreased with high Zn power of 60W and further dropped with Al doping. The decrease of transmittance in the NIR ranges was due to substation of Zn^{2+} with Al^{3+} which generates free electrons. The average transmittance T_a in the visible range between 400nm and 700nm of the AZO films are listed in Table 2. Undoped ZnO film (a) has the highest T_a of 82.9%. The films (c) and (d) deposited at L WD also displayed high T_a of 81.3% and 82.8%, respectively. The T_a for film (e) and (f) deposited at S WD decreased slightly to 72.5% and 71.6%, but their transmittance in the NIR dropped greatly below 5%.

The refractive index n and extinction coefficient k of the AZO films are shown in figure 3. The n in the visible region remains above 1.8 and the k remains nearly zero in the visible region, but n decreases and correspondingly k increases in the NIR range for all films except film (a). The film (f) has the smallest n of 0.7 and the highest k of 2.0 at the wavelength of 2500 nm. The lowest plasma wavelength λ_p (plasma wavelength is defined as a wavelength where n = k) is 1605 nm from the film (f).

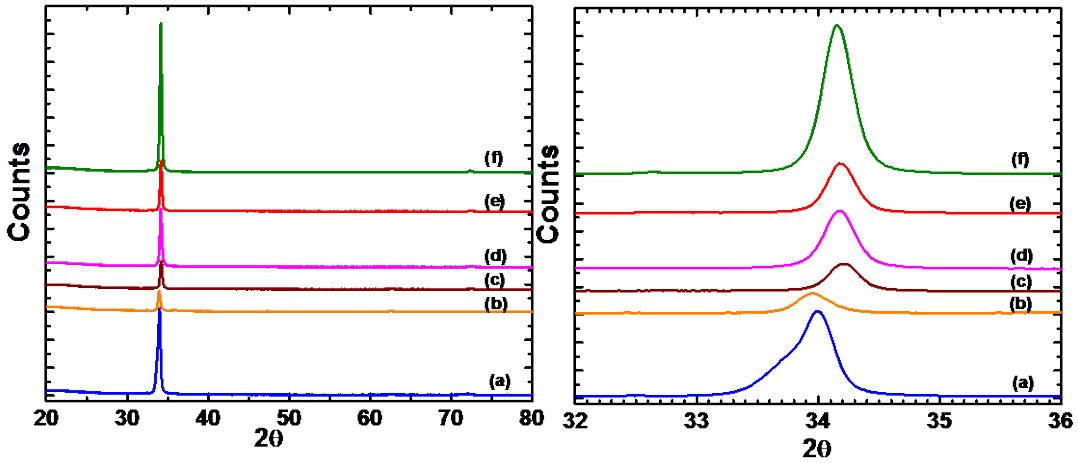

Figure 1 XRD patterns of the AZO films on quartz substrate

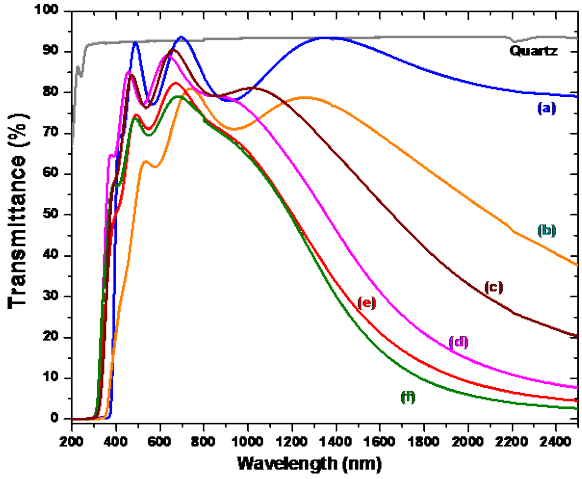

Figure 2 UV-Vis-NIR transmittance spectra of the AZO films

The electric resistivity ρ of the AZO films is also listed in Table 2. The undoped ZnO film (a) deposited at a low Zn power of 30W is a good insulator which ρ is more than 2 orders higher than that of the undoped ZnO deposited at a high Zn sputtering power of 60W. The ρ further decreased with Al doping. The film (f) has the lowest ρ of $9.87x10^{-4}$ Ω·cm, and correspondingly the shortest λ_p of 1605nm.

Table 2.

Sample	Al/(Al+Zn) (%)	(002) position	(002) FWHM	T_a (%)	λ_p (nm)	ρ (Ω·cm)
(a)	0	34.00	0.435	82.9		$1.58 x10^{0}$
(b)	0	33.96	0.312	57.1		$9.13x10^{-3}$
(c)	5.4	34.20	0.271	81.3	2540	$3.93 x10^{-3}$
(d)	7.8	34.17	0.287	82.8	1876	$1.35 x10^{-3}$
(e)	4.5	34.17	0.259	72.5	1653	$1.54 x10^{-3}$
(f)	6.3	34.15	0.282	71.6	1605	$9.87 x10^{-4}$

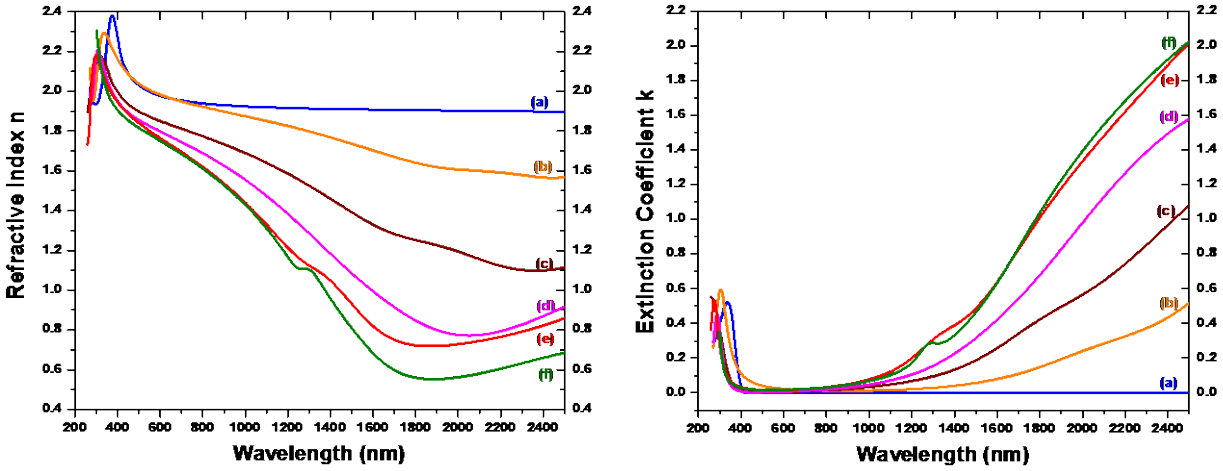

Figure 3 Refractive index n (left) and extinction coefficient k of (right) the AZO films.

4. Conclusions

AZO films were deposited using reactive magnetron co-sputtering. The transmittance of the AZO films in the NIR range can be controlled by adjusting Al doping content during deposition. The deposited AZO films show high transparency in the visible region and low transmittance in the NIR range. The AZO film deposited at a long WD and at heated substrate of 170˚C shows high transparency with high average transmittance of 82.8% in the visible range of 400-700nm and high conductivity with low electric resistivity of $1.35x10^{-3}$ Ω·cm.

5. Reference

[1] Doo-Soo Kim, Ji-Hyeon Park, Su-Jeong Lee, Kyung-Jun Ahn, Mi-So Lee, Moon-Ho Ham, Woong Lee, Jae-Min Myoung, “Effects of oxygen concentration on the properties of Al-doped ZnO transparent conductive films deposited by pulsed DC magnetron sputtering”, Materials Science in Semiconductor Processing 16 (2013) 997-1001.
[2] Y. Okuhara, H. Matsubara, C. Numako and M. Takata, ”Effective doping of Al in ZnO films by multi-target reactive sputtering for near-infrared reflection”, Journal of the Australian Ceramic Society Volume 49[1], 2013, 15-20.
[3] Y. Okuhara, T. Kato, H. Matsubara, N. Isu, M. Takata, “Near-infrared reflection from periodically aluminum-doped zinc oxide thin films”, Thin Solid Films 519 (2011) 2280-2286.
[4] R. Das and S. Ray, “Zinc Oxide – a transparent, conducting IR-reflector prepared by rf-magnetron sputtering”, J. Phys. D: Appl. Phys. 36 (2003) 152-155.
[5] Z.C. Jin, I. Hamberg and C.G. Granqvist, “Optical Properties of sputtered ZnO:Al thin film”, J. Appl. Phys. 64(10), (1988) 5117-5131.
[6] A. Barhoumi, G. Leroy, B. Duponchel, J. Gest, L. Yang, N. Waldhoff, S. Guermazi, “ Aluminum doped ZnO thin films deposited by direct current sputtering: Structural and optical properties”, Superlattices and Microstructures 82 (2015) 483-498.